BRILLOUIN SCATTERING AS A TOOL FOR CHARACTERIZING SURFACES, INTERFACES AND THIN FILMS

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INTRODUCTION

In the past decade, considerable progress has been made in the development of Brillouin scattering (BS) as a technique for the nondestructive characterization of materials. With the advent of high resolution and high contrast multipass tandem Fabry-Perot interferometry [1], BS has been applied to the measurement of the near-surface elastic properties of opaque materials [2], thin supported films [3] and interfaces [4], making use of various guided and localized acoustic modes including Rayleigh waves, pseudo-surface acoustic waves (p-SAW), Sezawa waves and Stoneley waves. By identifying the presence of particular acoustic modes in BS spectra, and comparing these with calculation, one can extract information pertaining to the physical properties of the system.

Brillouin scattering is the inelastic scattering of light by thermally excited phonons. For opaque materials the scattering occurs at or near the surface and is usually mediated by the surface ripple mechanism [5], and is sensitive to the dynamic response of a few hundreds of atomic layers of the surface. It is an ideal technique for characterizing thin films and near surface properties affected by radiation damage, ion-implantation and ion exchange, mechanical polishing and other surface modifications. The use of conventional ultrasonic techniques in these situations is difficult because of the large wave length in relation to the film thickness. Brillouin scattering is also a valuable NDE technique for the characterization of materials at high temperatures [6] and pressures.

Review of Progress in Quantitative Nondestructive Evaluation, Vol. 17
Edited by D.O. Thompson and D.E. Chimenti,, Plenum Press, New York, 1998

In order to demonstrate the potential of Brillouin scattering as a tool for the NDE of materials, we report some recently obtained results from our laboratory. We have conducted measurements of the SAW velocity of TiN hard films on steel as a function of film thickness, nitrogen partial pressure used in the deposition process, and temperature. This is an example of a fast on slow system in which the layer has the effect of increasing the SAW velocity over that of the substrate. Good correlation has been found between the SAW velocity and residual stress and adhesion force (critical load) of the films. From these measurements, we have obtained information about the variation of the effective elastic constants of TiN with film thickness, and for thick films, as a function of temperature. From measurements on single crystal silicon, the three independent elastic constants have been extracted using the dependence of the SAW velocity on wave propagation direction (angular dispersion) at temperatures up to 800°C. We also report the elastic properties of amorphous silicon layers formed by Ar-ion bombardment of the (001) silicon surface. This is a case of a slow on fast system in which the layer has the effect of decreasing the SAW velocity.

EXPERIMENT DETAILS

Brillouin scattering was performed using an argon-ion laser in a single axial mode with a wavelength of λ_i=514.5nm and output of 300-450 mW. In surface Brillouin scattering (SBS) from opaque materials the relevant acoustic excitations are confined to the near surface region, resulting in the conservation of wavevector component parallel to the surface. For the back-scattering geometry in our experiments the phonon (surface vibrational excitation) wavevector $k_{\|}$ is given by

$$k_{\|} = 2k_i \sin\theta, \tag{1}$$

where k_i is the wavevector of the incident light and θ is the incidence angle with respect to the surface normal. The phase velocity of the surface wave is related to the frequency shift f_B in the SBS spectrum by

$$v = \lambda_i f_B / 2\sin\theta. \tag{2}$$

The inelastically scattered light is resolved with a (3+3) pass tandem Fabry-Perot interferometer, and then detected by a cooled photomultiplier tube with less than one dark count per second and finally accumulated in a multichannel analyzer as the Brillouin spectrum.

The SAW velocity as a function of wave propagation direction or angular dispersion relation was measured by rotating the sample around its normal. For room temperature measurements of TiN on steel and amorphous layer on silicon, the samples were kept in air and the incident light was focused on the surface by a 50mm focal length lens of aperture f/2.3. In the back scattering geometry, the scattered light was collected by the same lens. For high temperature measurements the samples were mounted in a specially designed optical furnace with rotatable sample holder and a 120-mm focal length lens of aperture f/5.3 was used to illuminate the sample and collect the scattered light. The sample temperature was monitored by a thermocouple placed adjacent to the sample. A

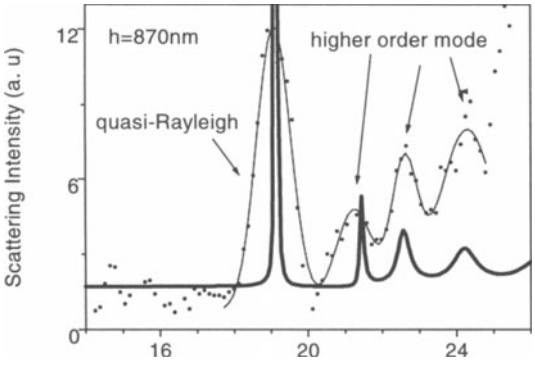

Figure 1. Comparison between the measured and calculated Brillouin spectra for the TiN film of thickness 870nm on high speed steel. In the figure, the thin solid line is the Gaussian fitting of the measured data (the dots), and the thick line is the calculated spectrum.

temperature controller was used to maintain thermal stability of better than 1°C during the rather lengthy measurement series.

Sample Preparation

Samples of TiN films were deposited on both mild and high speed steel in Ar/N_2 plasma by a hollow cathode discharge plating technique or magnetron sputtering. Various states of stress and composition in TiN_x films were obtained by altering the nitrogen partial pressure in the deposition process from 6.7×10^{-3} to 6.0×10^{-1} Pa., while keeping the substrate at temperature 500°C and negatively biased at -50V. The TiN films were mechanically polished to a flatness of 0.05μm using diamond and Al_2O_3 polishing powders in order to reduce the elastic scattering of light and detect the weak inelastic scattering peaks in the spectrum. The samples of single crystal silicon were chemically polished. Amorphous layers were formed by Argon ion bombardment at room temperature with ion energies ranging from 30 keV to 150 keV, and total ion current maintained at 30 μA and relatively high fluency of $1x10^{17}$ ions/cm^2. The amorphous nature of the layers is confirmed by Brillouin scattering measurements which show a suppression of the angular dispersion of the SAW velocity on the bombarded surface.

RESULTS AND DISCUSSION

TiN Films on Steel

A series of BS measurements of SAW velocity as a function of film thickness for TiN films on high speed steel have been reported [7]. In this strong stiffening system, guided modes take the form of true SAW, highly damped p-SAW, "pre-Rayleigh" and "quasi-Rayleigh" and its higher order modes as the film thickness increases. Figure 1 shows the comparison between the measured and calculated spectrum for the 870nm film. The

known bulk properties of TiN and steel were used in the calculation [8]. There is good agreement between the measured and calculated peaks' positions. In addition to the quasi-Rayleigh waves, higher order acoustic modes are also observed. For the thick films, the substrate has little effect on the SAW velocity, and the acoustic mode is very close to the

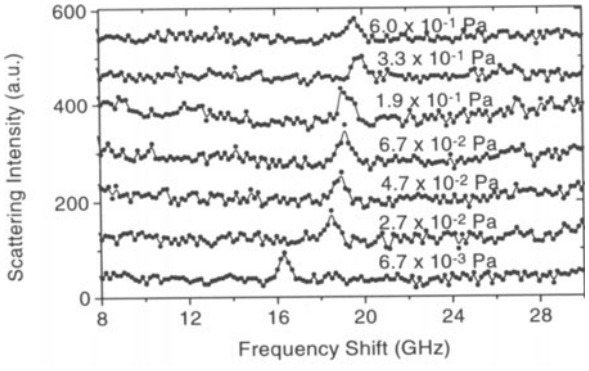

Figure 2. Measured Brillouin scattering peaks as a function of the nitrogen partial pressure during deposition.

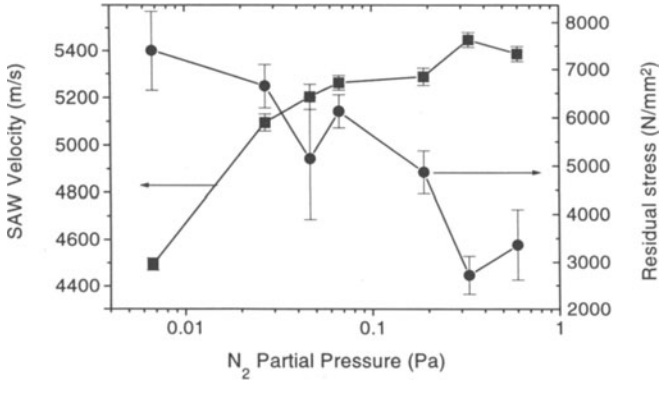

Figure 3. Correlation between the measured SAW velocity and residual stress in 3.5μm TiN films.

Rayleigh wave of bulk TiN. The measured SAW velocities for the thinner films with thickness<500nm indicate a reduction in the effective elastic moduli of the TiN films as compared with those of bulk TiN. This reduction is caused, most likely, by compositional variations at the interface.

The elastic constants of thick TiN films at temperatures up to 600°C were obtained from measured SAW velocities [9]. There is a downward trend of the SAW velocity and hence elastic moduli with increasing temperature.

We have also carried out BS measurements on TiN_x films on mild steel as a function of the deposition nitrogen partial pressure. All the films in these measurements were 3.5μm thick, a typical thickness in tool coating applications. Figure 2 shows the measured inelastic scattering peak in the spectra as a function of the deposition nitrogen partial pressure. The SAW velocity and residual stress in the films are shown in figure 3. The measured SAW velocity increases as the N_2 partial pressure increases in the range of 6.7×10^{-3} to 3.3×10^{-1} Pa, and then decreases slightly for larger N_2 pressure. The lattice parameter and preferred orientation of the TiN_x films were measured using X-ray

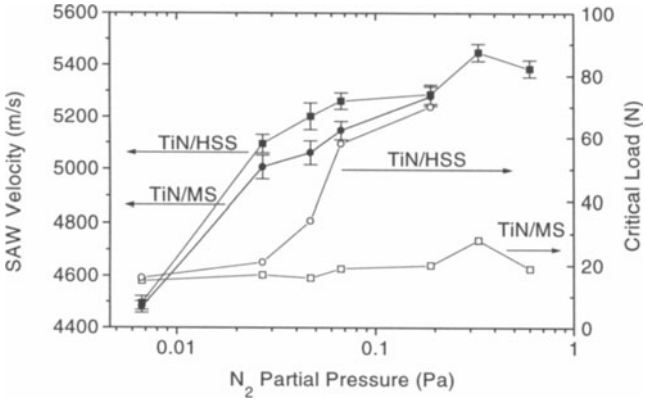

Figure 4. Correlation between the measured SAW velocity and critical load of 3.5μm TiN films on both high speed and mild steel. The SAW velocity is insensitive to the substrate due to the large film thickness.

diffraction and the compressive residual stress determined using the $\sin^2\Psi$ method [10]. The residual stress in the films has a trend opposite to that of the SAW velocity. The good correlation indicates that Brillouin scattering can be used as a nondestructive method for investigating the stress states of coatings.

The adhesion force of the film to the substrate is measured by the critical load method. The critical load L_c is defined as the smallest load at which the film is damaged when an increasingly loaded diamond stylus is drawn across the film. The damage is judged by emitted acoustic signals. The measured SAW velocities and critical loads for the TiN films on both mild and high speed steel are shown in figure 4, in which it can be seen that the saw velocity has the same trend as that of the critical load, at least for the combination of TiN on high speed steel. The values of critical load for the film on high speed steel

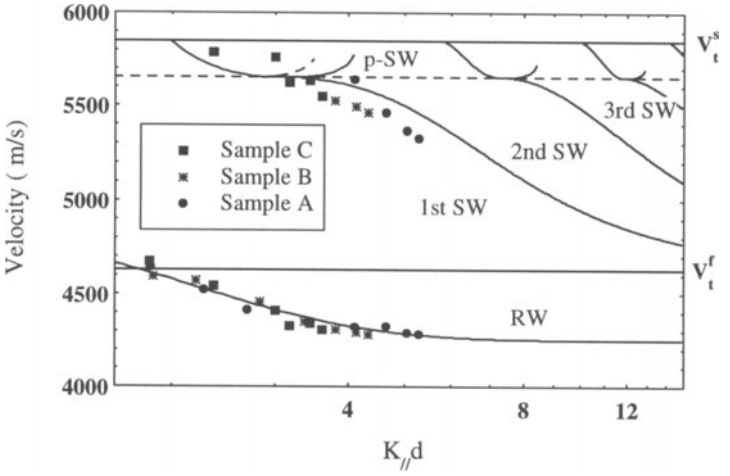

Figure 5. Dispersion relations for an isotropic amorphous Si layer on the (001) plane of silicon crystal, the measurements being taken along the [100] direction. The solid curves are the calculated dispersion relations, and RW stands for Rayleigh wave, SW for different order Sezawa waves and p-SW for pseudo-Sezawa waves. The p-SW's appear above the transonic state represented by the dashed line.

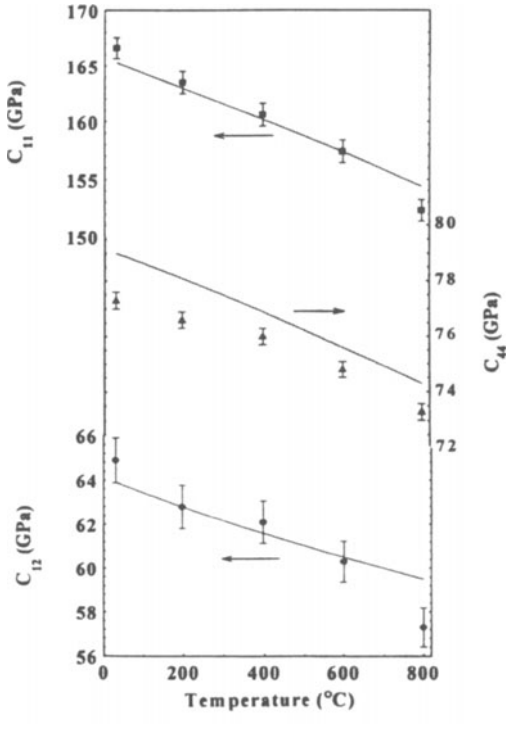

Figure 6. Comparison between the elastic constants measured ultrasonically (the lines) and obtained by least squares fitting of the BS measured SAW velocities.

are much different from the film on mild steel.This is likely due to the fact that the mild steel is much softer than the high speed steel and therefore tends to deform plastically under the applied load, leading to earlier crack propagation in the films and therefore coating failure at lower loads. It is clear from the BS measurements that there is good mechanical contact between the TiN and substrate, since otherwise the SAW velocity would drop below that of the substrate for the thinner films [9].

Amorphous Layer on Silicon Crystal

We have also conducted Brillouin scattering measurements of acoustic excitations in an Ar-ion bombarded silicon crystal along the [001] direction in the (001) surface, by varying the scattering angle and therefore $k_{\parallel}$. The thickness of the amorphous layer, which we treat as uniform and isotropic, was controlled by varying the ion energy. The acoustic modes measured in this slow on fast system are the Rayleigh wave, and the Sezawa and pseudo-Sezawa waves as shown in figure 5. The Sezawa and pseudo-Sezawa waves appear above critical values of $k_{\parallel}h$

High Temperature Elastic Constants of Silicon

Brillouin spectra were measured on the (001) surface of a silicon single crystal as a function of propagation direction at temperatures up to 800°C [11]. Using a least squares fit to the measured angular dependence of the SAW velocities, the three independent elastic constants of silicon crystal were obtained at high temperatures as shown in figure 6. Both the absolute values and the temperature dependence agree reasonably well with earlier ultrasonic results [12]. The small discrepancies could be due to the presence (on the silicon surface) of a thin oxide layer, which could cause a slight reduction in the measured SAW velocities.

Interfacial Modes

We have begun to characterize supported thin polycrystalline film systems through the study of the acoustic response at both the substrate/film interface and free film surface. Work has been done on simple metal films supported by transparent crystalline and amorphous substrates. We have also examined Ni/V multilayers on float glass intended as neutron monochromators. In all cases we have obtained reasonable agreement with calculated velocities. Brillouin scattering investigations of opaque materials in a diamond anvil pressure cell are underway.

ACKNOWLEDGMENTS

The authors are grateful to the Atomic Energy Corporation Ltd. of South Africa for allowing the use of their facilities for the preparation of the TiN films. The work was partially financially supported by the Foundation for Research and Development, South Africa.

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